



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 099 746 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**22.03.2006 Bulletin 2006/12**

(51) Int Cl.:  
**C10J 3/02** <sup>(2006.01)</sup> **C10J 3/57** <sup>(2006.01)</sup>  
**C22B 7/00** <sup>(2006.01)</sup> **H01M 10/54** <sup>(2006.01)</sup>  
**B09B 3/00** <sup>(2006.01)</sup> **F23G 5/027** <sup>(2006.01)</sup>

(21) Application number: **00830734.0**

(22) Date of filing: **07.11.2000**

(54) **Continuous process for transforming material and apparatus apt to carry out such process**

Kontinuierliches Verfahren zur Transformierung von Materialien und Vorrichtung dafür

Méthode en continu pour la transformation de matériau et appareillage à cet effet

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR**

• **Colletta, Angelo,**  
**Centro Sviluppo Materiali S.p.A.**  
**00129 Roma RM (IT)**

(30) Priority: **10.11.1999 IT RM990692**

(74) Representative: **Leone, Mario et al**  
**Società Italiana Brevetti S.p.A.**  
**Piazza di Pietra 39**  
**00186 Roma (IT)**

(43) Date of publication of application:  
**16.05.2001 Bulletin 2001/20**

(73) Proprietor: **CENTRO SVILUPPO MATERIALI S.p.A.**  
**00129 Roma (IT)**

(56) References cited:  
**WO-A-98/04751** **DE-A- 19 720 420**  
**GB-A- 2 103 648** **US-A- 5 885 322**

(72) Inventors:  
• **Granati, Paolo,**  
**c/o Centro Sviluppo Materiali SpA**  
**00129 Roma RM (IT)**

**EP 1 099 746 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

**[0001]** The present invention relates to a continuous process for transforming, by chemico-physical reactions inside molten slag, materials to be gasified, thermally destroyed, inertized or from which elements of commercial value are to be recovered, yielding controlled composition products, and to an apparatus apt to carry out such process.

**[0002]** WO 98/04751 discloses a process for direct production of cast iron from iron bearing ore in an apparatus having two chamber. The iron bearing ore and oxygen are introduced in the upper chamber, while oxygen, coal and flux are introduced in the lower chamber.

**[0003]** DE 197 20 420 A1 refers to an apparatus having a reaction chamber with two portion: a top slag portion and a bottom molten metal portion. Oxygen, fuel and the metal oxides to be transformed are injected onto the melt via a vertical lance, additional fuel and oxygen are injected via nozzles into the bottom part of the reactor.

**[0004]** Also in the apparatus of US 5885322, where a similar process is carried out, the introduction of iron oxide, oxygen, nitrogen and fuel takes place onto the molten slag.

**[0005]** In the process and apparatus of GB 2103648A an overhead lance is used to inject oxidizing gas onto the melt, whereas the carbonaceous material to be gasified is injected onto the melt through a lance or a tuyere.

**[0006]** In particular, the present invention relates to a process and to an apparatus comprising a reaction chamber, called reactor, for the continuous transforming by chemico-physical reactions inside molten slag of solid, liquid and gaseous material, even of scrap, yielding controlled composition products at the output of the apparatus itself, avoiding difficult to recycle and/or harmful by-products.

**[0007]** The process object of the present invention is a continuous process for transforming, by chemico-physical reactions inside molten slag, a material - even scrap - yielding a controlled composition product, carried out in an apparatus comprising a reaction chamber, called reactor, having a substantially cylindrical symmetry, including two portions, a top one and a bottom one, communicating and functionally distinct therebetween, said process comprising the steps of:

- possibly, introducing sideways in the top portion of the reactor, through a first injection level, a comburent gas for the post-combustion of the process gases;
- possibly, introducing inert stirring gases from the reactor bottom;
- extracting the process gases from the top portion of the reactor;
- tapping the transformed material of controlled composition and the inert slag from the bottom portion of the reactor, and
- being characterised by the fact of introducing, jointly and concomitantly, in the bottom portion of the reactor, directly into the molten slag, sideways through a second injection level and vertically from the top thereof, or only vertically from the top thereof, the material to be gasified, thermally destroyed, inertized or from which elements of commercial value are to be recovered, the fuel, the comburent, and possibly slag inoculants and additives and material-carrying gases.

**[0008]** The introduction into the bottom portion of the reactor of the material to be transformed, the fuel, the comburent, the possible inoculants and additives and the material-carrying gases can be carried out sideways and vertically from the top thereof. The sideways introduction into the bottom portion of the material to be transformed, together with the fuel, the comburent and the additives, can also be carried out in the radial direction through a plurality of inlets, possibly on different levels.

**[0009]** In an embodiment of the present invention, the material to be transformed, the fuel, a fraction of the comburent, the possible inoculants, additives and material-carrying gases, are introduced into the reactor towards the slag core by horizontal or downwards-slanting injection, and, concomitantly, the remaining comburent fraction is introduced therein with injectors at an upper level.

**[0010]** The material to be transformed may have a granulometry lower than 8 mm.

**[0011]** The granulometry of the fuel and of the additives may be lower than 3 mm.

**[0012]** The injection rate of the comburent into the top portion is lower than 40 m/s, and anyhow such as to allow the individual jets to intermingle thereamong, an effective combustion of the process gas inducted from the bottom portion of the reactor, and the yield of a heat transfer efficiency (HTE) greater than 70% between the gas and the molten metal bath.

**[0013]** In embodiments of the process according to the invention the binary basicity index of the slag is greater than 1.

**[0014]** The formation of a slag phase/metal phase emulsion in the bottom portion of the reactor for attaining an efficient heat transfer and elevated reaction kinetics may also be carried out with the injection of stirring gas from the reactor bottom, the power provided by the stirring gas being lower than 2.5 kW per ton of molten metal bath.

**[0015]** The internal pressure of the reactor may range from 1 to 4 bars.

**[0016]** A further subject-matter of the invention is an apparatus for the above continuous transforming, by chemico-physical reactions inside molten slag, of materials to be gasified, thermally destroyed, inertized, or from which elements

of commercial value are to be recovered, yielding controlled composition products, comprising:

- a reaction chamber, called reactor, having a substantially cylindrical symmetry, including two portions, a top and a bottom one, communicating and functionally distinct therebetween for carrying out the process;
- a substantially frustoconical-shaped connector, between the top portion of the reactor and a flue gas ejection conduit;
- possibly, means for injecting the comburent in order to carry out the post-combustion of the process gases;
- a tap hole for the transformed material and the slags yielded;
- possibly, means for feeding the stirring gas onto the reactor bottom,

characterised by the fact of having means for feeding, jointly and concomitantly, into the bottom portion of the reactor, directly into the molten slag, sideways and vertically from the top of the reactor or only vertically from the top, the material to be transformed, the fuel, possibly the slag inoculants and additives, and the material-carrying gases,

**[0017]** The means for the joint and concomitant feeding of the material to be transformed, the fuel, the comburent and the additives to the bottom portion of the reactor may be nozzles, circumferentially arranged, horizontal or slanting downwards, and oriented centerwise, and of at least one lance, vertically arranged so as to directly inject into the molten slag.

**[0018]** Said nozzles may be slanting downwards of an angle ranging from 0 to 40° with respect to the horizontal plane.

**[0019]** The ratio between the inside height and the inside diameter of the cylindrical chamber, reactor, may range from 1 to 8.

**[0020]** The ratio between the heights of the frustoconical-shaped connector and of the reactor may range from 0.2 to 0.5. The means for feeding the stirring gas into the reactor may be porous baffles located onto the bottom thereof.

**[0021]** The cylindrical top portion of the reactor may be differentially cooled along the height thereof.

**[0022]** The materials to be thermally destroyed, gasified, inertized, or from which products of commercial value are to be recovered are inletted into the reactor, in the portion thereof with the molten slag bath, through a plurality of nozzles, and possibly carried by a material-carrying gas, concomitantly and jointly to the slag additives and inoculants (like, e.g., calcium or magnesium oxides or carbonates), possibly highly reducing metals (like, e.g., aluminium, magnesium), fuel (like pit coal, fuel oil, natural gas or binary or ternary mixtures thereof) and to the comburent (like air, oxygen or a mixture thereof).

**[0023]** The material inletted into the slag meets an elevated temperature environment which, owing to the presence of the fuel carbon and of the carbon monoxide evolved from the partial burning of the fuel with the comburent gas, and to that of possible injected reducing metals, is highly reducing.

**[0024]** All the above leads to a ready reduction of the reducible metallic oxides, like iron, chromium, nickel and lead oxides, and to the evaporation of volatile metals like zinc, lead and cadmium.

**[0025]** The presence of calcium oxide in the slag and the highly reducing environment, needwise enhanced by the reducing metals injected therein, entails that the harmful elements (like, e.g., sulfur and halogens) be incorporated in the slag essentially as calcium salts; the reducing environment avoids the formation of NO<sub>x</sub> in the process flue gases.

**[0026]** The non-reducible oxides, like CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, are completely incorporated, since they dissolve in the slag.

**[0027]** The direct gasification under reducing conditions of the injected carbon-containing materials provides CO; further CO may evolve from the reduction of metallic oxides by the slag-dispersed carbon; the process gas thus evolved may possibly be post-combusted, in order to sustain the thermal state of the reactor, even injecting comburent therein through upperly located nozzles.

**[0028]** The processes implementable according to the present invention in view of the aims thereof require elevated reaction kinetics, depending also on an adequate homogeneity of the bath (made of metallic and of slag phases), and efficient heat exchanges, aims to be attained with a intensive bath stirring.

**[0029]** The bath stirring is essentially carried out by the materials injected with the abovementioned nozzles, and possibly by blowing gas from the reactor bottom.

**[0030]** Hence, the apparatus subject-matter of the present invention provides elevated operative flexibility and specific productivity.

**[0031]** So far, a general description of the present invention has been provided. With the aid of the figure and of the following examples, a detailed description of its embodiments, aimed at making better understood its tasks, features, advantages and operation modes, will hereinafter be provided.

**[0032]** Figure 1 schematically shows the section of an embodiment of the apparatus according to the present invention.

**[0033]** The apparatus shown in Figure 1 is made of a substantially cylindrical reactor body 1, having two portions, a top portion 2 and a bottom portion 3, communicating and functionally distinct therebetween for carrying out the process, connected, with a frustoconical-shaped connector 4, to a flue gas ejection conduit 5 (partially illustrated in the Figure) destined to outlet the process flue gases.

**[0034]** In the bottom portion 3 of the reactor, at least one level of slag injectors is located, for the concomitant and

joint introduction of the materials to be treated, the fuel, the comburent, the slag additives and inoculants and the carrier gases. The injection is carried out through a plurality of nozzles 6 (two thereof shown in the Figure) circumferentially arranged, with a radial direction of injection, and also through at least one lance 7, vertically arranged so as to directly inject into the slag.

5 [0035] In order to carry out a possible post-combustion, in the top portion 2 of the reactor the injection of comburent through a plurality of nozzles 8, circumferentially arranged, injecting in the radial direction, horizontal or slanting bottom-wise (only two thereof shown in Figure), is provided.

[0036] Furthermore, in the bottom portion 3 of the reactor a tap hole 9, and the related evacuation system, is provided, through which the tapping of the hot metal 10 and of the molten slag 11 is carried out.

10 [0037] In light of the aims of elevated efficiency of the chemical reactions and of flexibility and productivity of the reactor, elevated reaction kinetics are required, the latter also depending on An adequate homogeneity of the bath (made of metal and slag phases) and on efficient heat transfers. These aims are to be attained by intensive bath stirring.

[0038] The bath stirring is essentially carried out by the materials injected with carrier gases through the nozzles 6, through the lance 7 and by the comburent gas injected through the nozzles 8. An inert gas blowing from the reactor bottom with porous baffles (not shown in Figure) may also be provided therefor.

15 [0039] As it is apparent from the following examples, the embodiment of the reactor remains substantially unchanged for processes of different nature. Thus, the flexibility of the plant for processes with different technological aims, yet all based on the same principle of slag phase reactions, is highlighted.

20 EXAMPLE 1

[0040] The features of the embodiment of the apparatus according to the invention used in this example are shown in the following table 1.1.

25 TABLE 1.1

D: reactor body inside diameter	2 m
H: overall reactor height (frustoconical shaped connector included)	5.8 m
Frustoconical-shaped connector height	2.3 m
Frustoconical-shaped connector spread	78°

30 [0041] In this example the above-identified plant is ran for the treatment of dusts yielded from electric arc furnace carbon steelmaking process (EAF dusts).

35 [0042] The introduced materials and the flow rates thereof (kg/h for the solids, Nm<sup>3</sup>/h for the gases) are shown in Table 1.2.

40 TABLE 1.2

EAF dusts from carbon steelmaking	3000 kg/h
Fuel	2064 kg/h pit coal
Primary comburent	1050 Nm <sup>3</sup> /h O <sub>2</sub>
Additives	143 kg/h MgO
Comburent for post-combustion	571 Nm <sup>3</sup> /h O <sub>2</sub>

45 [0043] The EAF dusts are injected, with inert gas, under the molten slag into the reactor, concomitantly and jointly to the pit coal, the oxygen and the magnesium oxide, through the lower level injectors.

50 [0044] The molten slag over the hot metal bath has a lower than 1600°C temperature so as to highly limit the evaporation of the metallic elements (like iron) and it will have a viscosity lower than 4 Poise at 1400° C so as to ensure an effective homogenising of the reaction environment.

[0045] Moreover, the slag composition should be such as to limit the wear of the refractory lining of the reactor (carbon-bonded magnesia refractories in the example) the percentage of magnesium oxide in the slag should be greater than 8%.

55 [0046] The binary basicity of the slag (%CaO/%SiO<sub>2</sub>) should range from 1 to 1.5.

[0047] Once injected in the slag, the mixture of EAF dusts, fuel and slag inoculants meets a high-temperature environment which is highly reducing due to the presence of gases evolved during the gasification of the fuel and of the

residual fuel left over.

[0048] All this leads to a ready reduction of the reducing metallic oxides in the mixture (e.g., iron, zinc, lead).

[0049] Owing to a bath temperature greater than 1450°C, the metals and the volatile oxides (like zinc and lead oxide) are completely exhausted (outletted) from the bath as vapours, to be subsequently recovered for the recycling thereof. The remaining metals, essentially iron, dissolve in the hot metal bath which is carburized by the fuel in excess dispersed into the molten slag phase.

[0050] The presence of calcium oxide in the charge and the highly reducing environment entail that the halogens and the harmful elements like sulfur are incorporated into the slag as calcium salts. The non-reducible salts (like CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) are completely retained in the bath, as they dissolve into the slag.

[0051] The combined fuel/comburent injection provides the energetic contribution required to carry out the process and to sustain the thermal state of the reactor. The control of the thermal state is carried out operating a partial post-combustion of the process gas injecting comburent through the upper level nozzles.

[0052] The stirring of the system (hot metal bath and molten slag) by blowing gas from the reactor bottom ensures the thermal and chemical bath homogeneity, increasing the process kinetics.

[0053] This operation mode yields a metal phase, a slag phase and a gaseous phase from the injected materials (EAF dusts, fuel, inoculants), which, by virtue of the filtering action of the slag, is essentially made of permanent gases (like nitrogen, carbon monoxide, carbon dioxide and hydrogen), steam and zinc and lead vapours. The resulting aeriform mix is free of harmful compounds (like SO<sub>x</sub>, NO<sub>x</sub>, chlorinated compounds and dusts).

[0054] The process gas continuously outletted from the reactor is piped to the zinc and lead recovery plants and to the recovery of the thermal energy contained therein.

[0055] The metal phase and the molten slag are intermittently tapped from the reactor opening the tap hole provided for the purpose.

[0056] The materials outletted from the apparatus are shown in Table 1.3.

TABLE 1.3

Flue gases outletted from the reactor	3000 kg/h
Tapped metal phase	750 kg/h
Tapped slag	1050 kg/h

[0057] Some of the quantities useful to define a proper carrying out of the process in terms of chemical reactions and heat exchange are shown in Table 1.4.

TABLE 1.4

Hot metal bath stirring power	0.5 kW/t of bath metal phase
Metal phase mass/Reactor slag mass ratio	1.0

EXAMPLE 2

[0058] The features of the embodiment of the apparatus according to the invention used in this example are analogous to those disclosed in the preceding Table 1.1.

[0059] The example relates to the use of the reactor for the carbon gasification finalised to the production of a CO- and H<sub>2</sub>-rich gas that be free of dusts, polluting or harmful compounds (sulfurated compounds, NO<sub>x</sub>s)

[0060] The inletted material and the flow rates thereof are shown in TABLE 2.1 (kg/h for the solids, Nm<sup>3</sup>/h for the gases)

TABLE 2.1

Powdered pit coal	3000 kg/h granulometry <100 μm
Comburent	2300 Nm <sup>3</sup> /h O <sub>2</sub>
Additives	150 kg/h (CaO + MgO)
Comburent for post-combustion	2300 Nm <sup>3</sup> /h O <sub>2</sub>

[0061] The coal gasification takes place in presence of a basic slag in a reducing environment, allowing on the one hand to incorporate in the slag as stable compounds the sulfur evolved from the coal gasification, on the other hand

solubilizing and readily inertizing the ashes resulting therefrom.

**[0062]** Moreover, the ready reduction of the metallic oxides (e.g., FeO<sub>x</sub>, MnO) in the ashes is obtained, and the metals thus yielded dissolve into the hot metal bath which is carburized by the fuel dispersed in the molten slag.

**[0063]** The in-slag gasification provides several advantages:

- the sulfur proneness to solubilize in the metal phase is opposed, hence the quality of the metal phase itself is improved;
- the quantity of sulfur in the process gas is kept at very low values, with the entailed environmental advantages;
- the presence of calcium oxide in the charge and the highly reducing environment entail the halogens and the harmful elements like the sulfur to be incorporated in the slag as calcium salts. The non-reducible oxides (like CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) are completely incorporated in the bath, as they dissolve in the slag;
- the presence of calcium oxide in an adequate concentration also allows the ready fixation as calcium silicates of the silica provided by the coal ashes, inertizing the latter; as an additional advantage, a local silica concentration in the slag is prevented, limiting the chemical attack to the refractories lining the injection nozzles.

**[0064]** The molten slag over the hot metal bath has a temperature lower than 1600°C so as to highly limit the evaporation of the metallic elements (like iron), and at 1400°C it will have a viscosity lower than 4 Poise, thus ensuring an effective blow-by and hence a remarkable homogeneity of the reaction environment.

**[0065]** Moreover, the slag composition should be such as to limit the wear of the refractories lining the reactor; in the example with carbon-bonded magnesia refractories, the percentage of magnesium oxide in the slag should be greater than 8%.

**[0066]** The binary basicity of the slag (CaO/SiO<sub>2</sub>) should range from 1 to 1.5.

**[0067]** The coal gasification carried out by the comburent concomitantly and jointly injected through the lower level injectors is finalised to the production of CO and H<sub>2</sub>.

**[0068]** In order to maintain the thermal state of the reactor, this gas may be partially post-combusted with comburent injected through the upper level injectors.

**[0069]** Needwise, in order to implement a thermal and chemical homogeneity of the bath apt to ensure elevated reaction kinetics, inert gas (e.g., N<sub>2</sub>) may be blown in the former from the reactor bottom.

**[0070]** This operation mode yields from the injected materials (pulverised pit coal, comburent, additives) a gaseous phase made of permanent gases (like nitrogen, carbon monoxide, carbon dioxide and hydrogen) and steam, free, by virtue of the filtering action of the slag, of harmful compounds like SO<sub>x</sub>, NO<sub>x</sub>, chlorinated compounds and dusts.

**[0071]** The process gas continuously outletted from the reactor is piped to recycling plants. The metal phase and the slag are intermittently tapped from the reactor opening the tap hole provided therefor.

**[0072]** The materials outletted from the apparatus are shown in Table 2.2.

TABLE 2.2

Flue gases outletted from reactor	6310 kg/h
Metal phase	100 kg/h
Slag	350 kg/h

**[0073]** The quantities useful to define a proper carrying out of the process, in terms of chemical reactions and of heat exchange, are shown in Table 2.3.

TABLE 2.3

Hot metal bath stirring power	0.5 kW/t metal phase of hot metal bath
Metal phase Mass/reactor slag mass ratio	1.0

**EXAMPLE 3**

**[0074]** The features of the embodiment of the apparatus according to the invention used in this example are analogous to those disclosed in the preceding Table 1 of Example 1.

**[0075]** The example relates to the use of the apparatus for the thermal destruction of Polychlorobenzene- (PCB-) containing materials, yielding CO, H<sub>2</sub> and chlorides of slag-fixed alkali-earth metals.

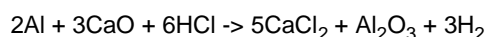
**[0076]** The inletted materials and the flow rates thereof (kg/h for the solids, Nm<sup>3</sup>/h for the gases) are shown in Table 3.1.

TABLE 3.1

PCB-containing materials	300 kg/h
Comburent	800 Nm <sup>3</sup> O <sub>2</sub>
Pit coal	600 kg/h
Additives	30 kg/h Al 130 kg/h CaO+MgO
Comburent for post-combustion	80 Nm <sup>3</sup> /h O <sub>2</sub>

**[0077]** In the use of the apparatus for the thermal destruction (present example) the aluminium is introduced from the top with the injection lance.

**[0078]** The slag having high liming activity, jointly to the presence of metallic aluminium, allows the PCB-like substances containing chlorine and hydrogen to yield hydrochloric acid, that is rapidly fixed in the slag according to the reaction:



and, under these conditions, the formation of harmful chlorinated gases like, e.g., phosgene, dioxins and polychlorofurans is avoided.

**[0079]** The thermodynamic activity of the lime in the slag should be greater than 0.05, and preferably ranging from 0.1 to 0.5.

**[0080]** Moreover, the slag composition should be such as to limit the wear of the refractories lining the reactor (in the example, carbon-bonded magnesia refractories). The percentage of magnesium oxide in the slag should be greater than 8%. In this case the working temperature of the slag ranges from 1600 to 1650°C.

**[0081]** This operation mode yields from the injected materials (PCB-containing materials, comburent and inoculants), a metal phase (essentially evolved from the metallic kinds in the carbon ashes) a slag phase and a gaseous phase which, by virtue of the filtering action of the slag, is essentially made of permanent gases (like nitrogen, carbon monoxide and hydrogen) and steam, free of harmful compounds (chlorinated compounds and dusts).

**[0082]** The process gas, continuously outletted from the reactor, is piped to the recycling plants.

**[0083]** The thermal state is controlled by operating a partial post-combustion of the process gas, injecting comburent through a second level of injectors.

**[0084]** The stirring of the system (hot metal bath and molten slag) obtained with the injection of the abovementioned materials and possibly by blowing gas from the reactor bottom, ensures the thermal and chemical homogeneity of the bath and allows elevated process kinetics.

**[0085]** The materials outletted from the apparatus are shown in Table 3.2.

TABLE 3.2

Flue gases outletted from reactor	2040 t/h
Metal phase	20 kg/h
Slag	250 kg/h

**[0086]** In Table 3.3, the quantities useful to define a proper carrying out of the process, in terms of chemical reactions and thermal exchange.

TABLE 3.3

Hot metal bath stirring power	0.5 kW/t of metal phase of hot metal bath
Metal phase mass/reactor slag mass ratio	1.0

#### EXAMPLE 4

**[0087]** The features of the embodiment of the apparatus according to the invention used in this example are analogous to those described in the preceding Table 1.1.

**[0088]** The example relates to the use of the apparatus for the treatment of Ni/Cd-containing scrap to be recovered.

**[0089]** The introduced materials and the flow rates thereof are shown in Table 4.1. (kg/h for the solids, Nm<sup>3</sup>/h for the

gases)

TABLE 4.1

Ni- and Cd-containing scraps	1000 kg/h granulometry <200 $\mu$ m
Comburent	800 Nm <sup>3</sup> /h O <sub>2</sub>
Fuel (pit coal)	770 kg/h
Additives	9 kg/h Al 60 kg/h (CaO+MgO)
Comburent	80 Nm <sup>3</sup> /h O <sub>2</sub>

**[0090]** The recycling of the Ni-Cd-containing scrap, also comprising Ni - Cd batteries, is carried out in presence of a basic slag, in a reducing environment and with process temperatures ranging from 1450 to 1600 °C. Such conditions also allow to fix in the slag as stable sulfides the sulfur evolved from the gasified carbon. The nickel oxide is completely reduced to metallic nickel, which, having a low vapour tension at 1600°C, accumulates in the metal phase together with the other metals, possibly extant as such in the charge or evolved from the reduction of the corresponding oxides extant therein. The cadmium, which vaporises at the operative temperature, is outletted with the process flue gases and recovered by downstream plants.

**[0091]** Thus, several advantages are obtained:

- quantitative separation of Ni and Cd;
- near-complete in-slag sulfur fixation, yielding a low-sulfur metal phase and a nearly sulfur-free process gas;
- the coal ashes are quantitatively fixed in the slag phase, by virtue of the filtering capacity of the slag itself. At 1400 °C the molten slag above the hot metal bath has a viscosity lower than 4 Poise, in order to ensure an effective homogeneity of the reaction environment.

**[0092]** The binary basicity of the slag (%CAO/%SiO<sub>2</sub>) ranges from 1 to 1.5.

**[0093]** Moreover, the slag composition should be such as to limit the wear of the refractories lining the reactor (carbon-bonded magnesia refractories in the example). The percentage of magnesium oxide in the slag should be greater than 8%.

**[0094]** The thermal state is controlled operating a partial post-combustion of the process gas injecting comburent through a second level of injectors.

**[0095]** The stirring of the system (hot metal bath and molten slag), obtained injecting the abovementioned materials and possibly blowing gas from the reactor bottom, ensures the thermal and chemical homogeneity of the bath and allows elevated process kinetics.

**[0096]** This operation mode yields from the injected materials (powdered pit coal, Ni-Cd battery scraps, fuel, additives) a gaseous phase made of Cd vapours, and, by virtue of the filtering action of the slag, of permanent gases (like nitrogen, carbon monoxide, carbon dioxide and hydrogen) and steam. The gaseous phase is free of harmful compounds like SO<sub>x</sub>, NO<sub>x</sub>, chlorinated compounds and dusts.

**[0097]** The process gas continuously outletted from the reactor is piped to the recycling plants. The metal phase and the slag are intermittently tapped from the reactor opening the tap hole provided therefor.

**[0098]** The materials outletted from the apparatus are shown in Table 4.2.

TABLE 4.2

Permanent gases	1835 kg/h
Metal phase	960 kg/h
Slag	100 kg/h
Gas-carried Cd	23 kg/h

**[0099]** The quantities useful to define a proper development of the process, in terms of chemical reactions and thermal exchange, are shown in Table 4.3.

TABLE 4.3

Hot metal bath stirring power	0.5 kW/t metal phase of hot metal bath
-------------------------------	--

Table continued

Metal phase Mass/reactor slag mass ratio	1.0
--	-----

5

**Claims**

10

1. A continuous process for transforming, by chemico-physical reactions inside molten slag, a material yielding a controlled composition product, in an apparatus comprising a reaction chamber (1), called reactor, having substantially cylindrical symmetry, including two portions, a top (2) and a bottom one (3), communicating and functionally distinct therebetween, said process comprising the steps of:

15

- possibly, introducing sideways into the top portion (2) of the reactor, through a first injection level, a comburent gas for the post-combustion of the process gases;
- possibly, introducing inert stirring gases from the reactor bottom;
- extracting the process flue gases from the top portion of the reactor;
- tapping from the bottom portion of the reactor the transformed material of controlled composition and the inert slag;

20

and being **characterised by** the fact of introducing, jointly and concomitantly, into the bottom portion (3) of the reactor, directly into the molten slag (11), sideways through a second injection level and vertically from the top thereof or only vertically from the top thereof, the material to be gasified, thermally destroyed, inertized or from which elements of commercial value are to be recovered, the fuel, the comburent and possibly slag inoculants and additives and material-carrying gases.

25

2. The transforming process according to claim 1, wherein the introduction into the bottom portion of the reactor of the material to be transformed, the fuel, the comburent, and possibly the slag inoculants and additives and the material-carrying gases, is carried out sideways and vertically from the top thereof.

30

3. The transforming process according to claim 1 or 2, wherein the introduction into the bottom portion of the reactor of the material to be transformed, the fuel, the comburent, and possibly the inoculants and additives and the material-carrying gases is carried out in the radial direction, with a plurality of inlets, possibly on different levels.

35

4. The transforming process according to any one of the claims 1 to 3, wherein in the bottom portion of the reactor the material to be transformed, the material-carrying gas, the fuel, a fraction of the comburent and possibly the inoculants and additives, are introduced at the slag core, horizontally or slanting downwards, and the remaining comburent fraction is concomitantly introduced at an upper level.

40

5. The transforming process according to any one of the preceding claims, wherein the material to be transformed has a granulometry lower than 5 mm.

6. The process according to any one of the preceding claims, wherein the granulometry of the fuel and of the additives is lower than 3 mm.

45

7. The process according to any one of the preceding claims, wherein the injection rate of the comburent into the top portion of the reactor is lower than 40 mis, and anyhow such as to allow the individual jets to intermingle thereamong and the combustion of the process gas inletted from the bottom portion of the reactor, and obtaining a heat transfer efficiency (HTE) greater than 70% between the gas and the bath.

50

8. The process according to any one of the preceding claims, wherein the binary basicity index of the slag is greater than 1.

55

9. The transforming process according to any one of the preceding claims, wherein the formation of a slag phase/metal phase emulsion in the bottom portion of the reactor is also carried out by injecting stirring gas from the reactor bottom, the power provided by the stirring gas being lower than 2,5 kW per ton of hot metal bath.

10. The process according to any one of the preceding claims, wherein the internal pressure of the reactor ranges from 1 to 4 bars.

11. An apparatus apt to carry out the continuous process of claims 1 to 10, for the continuous transforming, by chemi-co-physical reactions inside molten slag, of materials to be gasified, thermally destroyed, inertized or from which elements of commercial value are to be recovered, yielding controlled composition products, comprising:

- 5 - a reaction chamber (1), called reactor, of substantially cylindrical symmetry, having two portions, a top portion (2) and a bottom portion (3), communicating and functionally distinct therebetween for carrying out the process;
- a substantially frustoconical-shaped connector (4), between the top portion (2) and a flue gas ejection conduit (5);
- 10 - possibly means (8) for injecting the comburent in order to carry out the post-combustion of the process gases;
- a tap hole (9) for the transformed material (10) and the slag (11) yielded;
- possibly, means for feeding the inert stirring gas onto the reactor bottom,

15 **characterised by** the fact of having means (6,7) for feeding, jointly and concomitantly, into said bottom portion (3), directly into the molten slag, sideways and vertically from the top of the reactor or only vertically from the top of the reactor, the material to be transformed, the fuel, the comburent and possibly the slag inoculants and additives and the material-carrying gases.

20 12. The apparatus according to claim 11, wherein said means for feeding, concomitantly and jointly, the material to be transformed, the fuel, the comburent and possibly the inoculants and additives and the material-carrying gases, into the bottom portion of the reactor are nozzles, arranged circumferentially to said portion, horizontal or slanting downwards, and oriented centerwise, and at least one lance, vertically arranged so as to directly inject into the molten slag.

25 13. The apparatus according to claim 12, wherein said nozzles are slanting downwards of an angle ranging from 0 to 40° with respect to the horizontal plane.

14. The apparatus according to any one of the claims 11 to 13, wherein the ratio between the inside height of the reactor and the inside diameter thereof ranges from 1 to 8.

30 15. The apparatus according to any one of the preceding claims from 11 to 14, wherein the ratio between the height of the frustoconical-shaped connector and the height of the reactor ranges from 0.2 to 0.5.

35 16. The apparatus according to any one of the preceding claims 11 to 15, wherein said means for feeding stirring gas in said bottom portions of the reactor are porous baffles.

17. The apparatus according to any one of the preceding claims from 11 to 16, wherein the cylindrical top portion is differently cooled along the height thereof.

#### 40 **Revendications**

1. Procédé continu pour la transformation, par des réactions physico-chimiques au sein d'une scorie fondue, d'un matériau produisant un produit à composition contrôlée, dans un appareil comprenant une chambre de réaction (1), dénommée réacteur, présentant une symétrie substantiellement cylindrique, incluant deux parties, l'une haute (2) et l'autre basse (3), communiquant et fonctionnellement distinctes entre elles, ledit procédé comprenant les étapes consistant à :

- 45 - éventuellement, introduire latéralement dans la partie haute (2) du réacteur, à travers un premier niveau d'injection, un gaz comburant pour la post-combustion des gaz de traitement ;
- 50 - éventuellement, introduire des gaz inertes d'agitation depuis le bas du réacteur ;
- extraire les fumées du traitement depuis la partie haute du réacteur ;
- évacuer, depuis la partie basse du réacteur, le matériau transformé à composition contrôlée et la scorie inerte ;

55 et étant **caractérisé par** le fait d'introduire, conjointement et concomitamment, dans la partie basse (3) du réacteur, directement dans la scorie fondue (11), latéralement à travers un second niveau d'injection et verticalement depuis le haut de celui-ci ou seulement verticalement depuis le haut de celui-ci, le matériau à gazéifier, à détruire thermiquement, à rendre inerte ou duquel des éléments ayant une valeur commerciale doivent être récupérés, le combustible, le comburant et éventuellement des agents inoculants et additifs de la scorie et des gaz transportant des

## EP 1 099 746 B1

matériaux.

2. Procédé de transformation selon la revendication 1, dans lequel l'introduction au sein de la partie basse du réacteur du matériau destiné à être transformé, du combustible, du comburant et éventuellement des agents inoculants et additifs de la scorie et des gaz transportant des matériaux est effectuée latéralement et verticalement depuis le haut de celui-ci.
  3. Procédé de transformation selon l'une des revendications 1 à 2, dans lequel l'introduction au sein de la partie basse du réacteur du matériau destiné à être transformé, du combustible, du comburant et éventuellement des agents inoculants et additifs de la scorie et des gaz transportant des matériaux est effectuée selon la direction radiale, au moyen d'une pluralité d'entrées, éventuellement à différents niveaux.
  4. Procédé de transformation selon l'une des revendications 1 à 3, dans lequel, dans la partie basse du réacteur, le matériau destiné à être transformé, le gaz transportant des matériaux, le combustible, une fraction du comburant et éventuellement les agents inoculants et additifs sont introduits au coeur de la scorie, horizontalement ou de façon inclinée vers le bas, et la fraction de comburant restant est concomitamment introduite à un niveau supérieur.
  5. Procédé de transformation selon l'une des revendications précédentes, dans lequel le matériau destiné à être transformé présente une granulométrie inférieure à 5 mm.
  6. Procédé selon l'une des revendications précédentes, dans lequel la granulométrie du combustible et des additifs est inférieure à 3 mm.
  7. Procédé selon l'une des revendications précédentes, dans lequel le taux d'injection du comburant dans la partie haute du réacteur est inférieur à 40 m/s et en tout cas tel qu'il permet aux jets individuels de se croiser et à la combustion du gaz de traitement entré depuis la partie basse du réacteur de se produire, et à obtenir une efficacité de transfert de chaleur (HTE) supérieure à 70% entre le gaz et le bain.
  8. Procédé selon l'une des revendications précédente, dans lequel l'indice de basicité binaire de la scorie est supérieur à 1.
  9. Procédé de transformation selon l'une des revendications précédentes, dans lequel la formation d'une émulsion entre la phase de scorie et la phase de métal dans la partie basse du réacteur est aussi effectuée en injectant un gaz d'agitation depuis le bas du réacteur, la puissance fournie par le gaz d'agitation étant inférieure à 2,5 kW par tonne de bain métallique.
  10. Procédé selon l'une des revendications précédentes, dans lequel la pression interne du réacteur est comprise entre 1 et 4 bars.
  11. Appareil apte à réaliser le procédé continu selon l'une des revendications 1 à 10, pour la transformation continue, par des réactions physico-chimiques au sein d'une scorie fondue, de matériaux à gazéifier, à détruire thermiquement, à rendre inertes ou desquels des éléments ayant une valeur commerciale doivent être récupérés, produisant des produits à composition contrôlée, comprenant :
    - une chambre de réaction (1), dénommée réacteur, présentant une symétrie substantiellement cylindrique, possédant deux parties, l'une haute (2) et l'autre basse (3), communiquant et fonctionnellement distinctes entre elles, pour réaliser le procédé ;
    - un connecteur (4) de forme substantiellement tronconique, entre la partie haute (2) et un conduit (5) d'éjection de la fumée ;
    - éventuellement, des moyens (8) pour injecter le comburant de manière à effectuer la post-combustion des gaz de traitement ;
    - un trou de coulée (9) pour le matériau transformé (10) et la scorie (11) produits ;
    - éventuellement, des moyens pour amener le gaz inerte d'agitation sur le bas du réacteur ;
- caractérisé par le fait qu'il possède des moyens (6,7) pour amener, conjointement et concomitamment, dans ladite partie basse (3) directement au sein de la scorie fondue, latéralement et verticalement depuis le haut du réacteur ou seulement verticalement depuis le haut du réacteur, le matériau destiné à être transformé, le combustible, le comburant et éventuellement les agents inoculants et additifs de la scorie et les gaz transportant des matériaux.**

- 5 12. Appareil selon la revendication 11, dans lequel lesdits moyens pour amener, concomitamment et conjointement, le matériau destiné à être transformé, le combustible, le comburant et possiblement les agents inoculants et additifs et les gaz transportant des matériaux, au sein de la partie basse du réacteur sont des buses, disposées de manière circonférentielle à ladite portion, horizontalement ou inclinées vers le bas, et orientées de vers le centre, et au moins une lance, disposée verticalement de manière à injecter directement au sein de la scorie fondue.
- 10 13. Appareil selon la revendication 12, dans lequel lesdites buses sont inclinées vers le bas par rapport au plan horizontal, d'un angle compris entre 0 et 40 °.
- 15 14. Appareil selon l'une des revendications 1 à 13, dans lequel le rapport entre la hauteur interne du réacteur et le diamètre interne de celui-ci est compris entre 1 et 8.
- 15 15. Appareil selon l'une des revendications 11 à 14, dans lequel le rapport entre la hauteur du connecteur de forme tronconique et la hauteur du réacteur est compris entre 0,2 et 0,5.
- 20 16. Appareil selon l'une des revendications 1 à 15, dans lequel lesdits moyens pour amener le gaz d'agitation dans lesdites parties basses du réacteur sont des chicanes poreuses.
- 20 17. Appareil selon l'une des revendications 11 à 16, dans lequel la partie haute cylindrique est différemment refroidie le long de la hauteur de celle-ci.

### Patentansprüche

- 25 1. Kontinuierlicher Prozess zum Umwandeln eines Materials, das ein Erzeugnis mit gesteuerter Zusammensetzung ergibt, durch chemisch-physikalische Reaktionen im Inneren geschmolzener Schlacke in einer Vorrichtung, die eine Reaktionskammer (1), die als Reaktor bezeichnet wird, umfasst, die im Wesentlichen zylindrische Symmetrie aufweist und zwei Abschnitte, d.h. einen oberen (2) und einen unteren (3), enthält, die in Verbindung stehen und funktionell getrennt sind, wobei das Verfahren der folgenden Schritte umfasst:
- 30
- möglicherweise seitliches Einleiten eines Sauerstoffträgergases zur Nachverbrennung der Prozessgase in den oberen Abschnitt (2) des Reaktors über eine erste Einblasstufe;  
 möglicherweise Einleiten von inerten Spülgasen vom Boden des Reaktors;  
 Absaugen der Prozessabgase aus dem oberen Abschnitt des Reaktors;  
 35 Abstechen des umgewandelten Materials mit gesteuerter Zusammensetzung und der inerten Schlacke aus dem unteren Abschnitt des Reaktors;  
 wobei es durch die Tatsache **gekennzeichnet** ist, dass gemeinsam und gleichzeitig in den unteren Abschnitt (3) des Reaktors direkt in die geschmolzene Schlacke (11) hinein seitlich über eine zweite Einlassstufe und vertikal von der Oberseite desselben her oder nur vertikal von der Oberseite desselben her das Material, das vergast, thermisch zerstört, inertisiert werden soll oder aus dem Elemente mit wirtschaftlichem Wert zurückge-
- 40 gewonnen werden sollen, der Brennstoff, der Sauerstoffträger und möglicherweise Schlacke-Impfmittel und Zusätze sowie Material transportierende Gase eingeleitet werden.
- 45 2. Umwandlungsverfahren nach Anspruch 1, wobei das Einleiten des umzuwandelnden Materials, des Brennstoffs, des Sauerstoffträgers und möglicherweise der Schlacke-Impfmittel sowie -Zusätze und der Material transportierenden Gase in den unteren Abschnitt des Reaktors seitlich und vertikal von der Oberseite desselben her ausgeführt wird.
- 50 3. Umwandlungsverfahren nach Anspruch 1 oder 2, wobei das Einleiten des umzuwandelnden Materials, des Brennstoffs, des Sauerstoffträgers und möglicherweise der Impfstoffe und Zusätze sowie der Material transportierenden Gase in den unteren Abschnitt des Reaktors in der radialen Richtung mit einer Vielzahl von Einlassen, möglicherweise auf unterschiedlichen Stufen, ausgeführt wird.
- 55 4. Umwandlungsverfahren nach einem der Ansprüche 1 bis 3, wobei in dem unteren Abschnitt des Reaktors das umzuwandelnde Material, das Material transportierende Gas, der Brennstoff, ein Teil des Sauerstoffträgers und möglicherweise die Impfmittel und Zusätze in den Schlackekern horizontal oder schräg nach unten eingeleitet werden und der verbleibende Teil des Sauerstoffträgers gleichzeitig auf einer höheren Stufe eingeleitet wird.
5. Umwandlungsverfahren nach einem der vorangehenden Ansprüche, wobei das umzuwandelnde Material eine Korn-

größe von weniger als 5 mm hat.

6. Verfahren nach einem der vorangehenden Ansprüche, wobei die Korngröße des Brennstoffs und der Zusätze geringer ist als 3 mm.

7. Verfahren nach einem der vorangehenden Ansprüche, wobei die Einblasgeschwindigkeit des Sauerstoffträgers in den oberen Abschnitt des Reaktors niedriger ist als 40 m/s und in jedem Fall so, dass Vermischen der einzelnen Strahlen miteinander und die Verbrennung des Prozessgases, das über den unteren Abschnitt des Reaktors eingelassen wird, möglich sind und ein Wärmeübertragungswirkungsgrad von mehr als 70% zwischen dem Gas und dem Bad erreicht wird.

8. Verfahren nach einem der vorangehenden Ansprüche, wobei der binäre Basizitätsindex der Schlacke größer ist als 1.

9. Umwandlungsverfahren nach einem der vorangehenden Ansprüche, wobei die Ausbildung einer Schlackenphasen-Metallphasen-Emulsion im unteren Abschnitt des Reaktors ebenfalls ausgeführt wird, indem Spülgas über den Reaktorboden eingeblasen wird und die durch das Spülgas erzeugte Leistung weniger als 2,5 kW pro Tonne heißen Metallbades beträgt.

10. Verfahren nach einem der vorangehenden Ansprüche, wobei der Innendruck des Reaktors zwischen 1 und 4 bar liegt.

11. Vorrichtung, die geeignet ist, um das kontinuierliche Verfahren nach den Ansprüchen 1 bis 10 zur kontinuierlichen Umwandlung von Materialien auszuführen, die vergast, thermisch zerstört, inertisiert werden sollen oder aus denen Elemente mit wirtschaftlichem Wert zurückgewonnen werden sollen, durch chemisch-physikalische Reaktionen im Inneren geschmolzener Schlacke, so dass sich Erzeugnisse mit gesteuerter Zusammensetzung ergeben, wobei sie erfasst:

eine Reaktionskammer (1), die als Reaktor bezeichnet wird und im Wesentlichen zylindrische Symmetrie aufweist und zwei Abschnitte, d.h. einen oberen Abschnitt (2) und einen unteren Abschnitt (3) hat, die in Verbindung stehen und funktionell voneinander getrennt sind, um das Verfahren auszuführen;

einen im Wesentlichen kegelstumpfförmigen Verbinder (4) zwischen dem oberen Abschnitt (2) und einer Abgas-Ausstoßleitung (5),

möglicherweise eine Einrichtung (8) zum Einblasen des Sauerstoffträgers, um die Nachverbrennung der Prozessgase auszuführen;

ein Abstichloch (9) für das umgewandelte Material (10) und die Schlacke (11), die gewonnen werden;

möglicherweise eine Einrichtung zum Leiten des inerten Spülgases auf den Reaktorboden,

**gekennzeichnet durch** die Tatsache, dass sie Einrichtungen (6, 7) aufweist, die das umzuwandelnde Material, den Brennstoff, den Sauerstoffträger und möglicherweise die Schlacken-Impfmittel und -Zusätze sowie die Material transportierenden Gase gemeinsam und gleichzeitig in den unteren Abschnitt (3) direkt in die geschmolzene Schlacke hinein seitlich und vertikal von der Oberseite des Reaktors her oder nur vertikal von der Oberseite des Reaktors her einleiten.

12. Vorrichtung nach Anspruch 11, wobei die Einrichtungen, die das umzuwandelnde Material, den Brennstoff, den Sauerstoffträger und möglicherweise die Impfstoffe und Zusätze sowie die Material transportierenden Gase gleichzeitig und gemeinsam in den unteren Abschnitt des Reaktors einleiten, Düsen, die am Umfang des Abschnitts horizontal oder nach unten geneigt angeordnet und mittig ausgerichtet sind, und wenigstens eine Lanze sind, die vertikal angeordnet ist, so dass sie direkt in die geschmolzene Schlacke einbläst.

13. Vorrichtung nach Anspruch 12, wobei die Düsen in einem Winkel, der von 0 bis 40° reicht, in Bezug auf die horizontale Ebene nach unten geneigt sind.

14. Vorrichtung nach einem der Ansprüche 11 bis 13, wobei das Verhältnis zwischen der Innenhöhe des Reaktors und dem Innendurchmesser desselben zwischen 1 und 8 liegt.

15. Vorrichtung nach einem der vorangehenden Ansprüche von 11 bis 14, wobei das Verhältnis zwischen der Höhe des kegelstumpfförmigen Verbinders und der Höhe des Reaktors von 0,2 bis 0,5 reicht.

16. Vorrichtung nach einem der vorangehenden Ansprüche, wobei die Einrichtungen zum Einleiten von Spülgas in den unteren Abschnitt des Reaktors poröse Trennwände sind.

**EP 1 099 746 B1**

17. Vorrichtung nach einem der vorangehenden Ansprüche 11 bis 16, wobei der zylindrische obere Abschnitt entlang seiner Höhe unterschiedlich gekühlt wird.

5

10

15

20

25

30

35

40

45

50

55

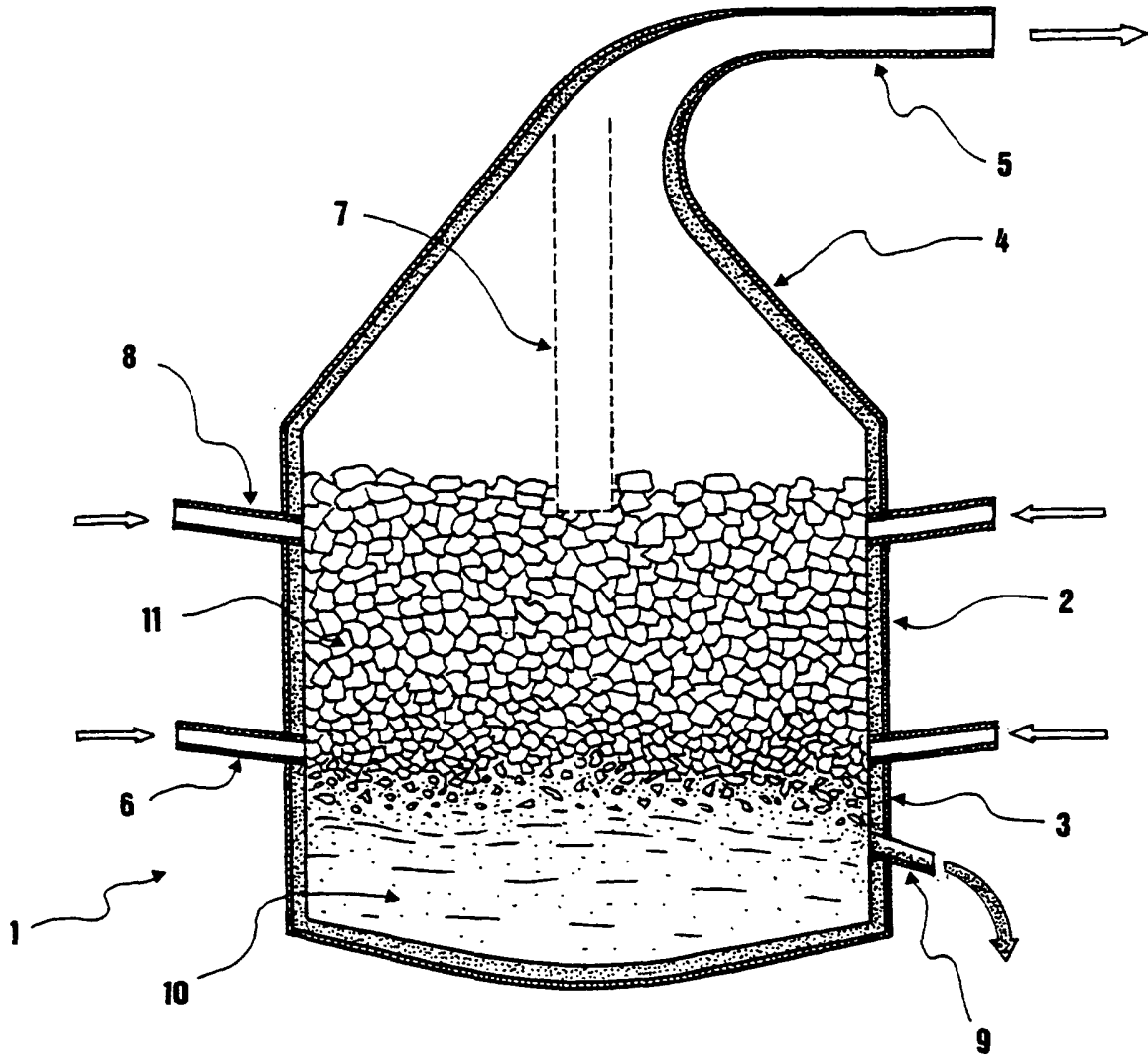


FIG.1